

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Method for Producing a Lime Hydrate.

We, G. & W. H. CORSON, INCORPORATED, a Corporation organized under the laws of the State of Delaware, United States of America, of Plymouth Meeting, Montgomery County, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to the production of commercial hydrated lime. More particularly, the invention is directed to an improved method of making a lime hydrate from a fast-acting quicklime. The term "fast-acting quicklime" as used herein means a quicklime which undergoes rapid hydration when contacted with water, the hydration or slaking time being below one minute and in many instances 5 seconds or less.

One of the essential properties of hydrated limes for use as mortars, plasters, and similar purposes is good plasticity. Plasticity, as it refers to a hydrated lime, is defined as the property which renders the hydrated lime capable of spreading easily on an absorbent surface, i.e., the plasticity depends directly upon the ability of the material in putty form to hold its water against the suction of an absorbent surface to which it is applied.

In order that a hydrated lime may be classified as a plastic finishing lime, it must so react with water as to produce a putty having a plasticity of 200 or greater as determined by the Emley plasticimeter as developed by the United States Bureau of Standards.

Certain requirements are essential to the

proper hydration of a quicklime in order for the resulting hydrate to have the desired degree of plasticity. To begin with, a large excess of water must be present at the time of hydration. By this is meant not that a large excess of water over that theoretically needed must be present at the start of the hydration of the mass of quicklime but that there must be water in the liquid phase available to practically every particle of the quicklime at the time that such particle of quicklime changes from the oxide form to the hydroxide form. It is well known that calcium oxide hydrated essentially in the presence of steam is extremely non-plastic.

With fast-acting quicklimes, hydration appears to take place at the surface of the particles; and the heat of hydration is so great that the water is converted to steam before it can penetrate the particles. In fact, with some very fast-acting quicklimes, the hydration reaction may be explosive in nature. Thus, the greater portion of such a quicklime is hydrated in an atmosphere of steam rather than being surrounded by water in the liquid phase. This is true even if considerably more water is used than is necessary to satisfy the chemical requirement of such a quicklime.

Attempts have been made to overcome this condition by endeavouring to prevent the temperature of the water from rising above 212° F. In such cases the hydration of the fast-acting quicklime is slowed down, and this has quite a detrimental effect on the plasticity of the resulting hydrated lime.

More recently, there have been suggested methods of hydrating a fast-acting quicklime to produce a lime hydrate having considerably improved properties, particularly plasticity. An especially advantageous

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method for hydrating such a quicklime is described in United States Patents 2,309,168 and 2,365,736.

According to these patents, water is mixed with the fast-acting quicklime, and the mixture is introduced into a hydration cylinder. In this cylinder the fast-acting quicklime is hydrated under pressure in the presence of water in the liquid state for a sufficient time to hydrate the calcium oxide content and the major portion of the magnesia content of such quicklime. When the hydration has been completed, the resulting wet slaked quicklime is dried by effecting a finely divided dispersive discharge from the hydration cylinder into an atmosphere capable of vaporizing substantially spontaneously the excess water carried by the quicklime particles as they are discharged, leaving a substantially dry, powdery hydrated lime. If the process according to these patents is of the continuous type, a slurry of the quicklime and water is continuously introduced into the hydration cylinder, and the resulting hydrated lime, water and steam are continuously discharged.

In such a process for hydrating a fast-acting quicklime, wherein water is mixed with the quicklime and the mixture is conveyed to the hydration cylinder, fast-acting quicklimes which have an essentially instantaneous hydration time, e.g., a hydration time of 5 seconds or less are extremely difficult to handle. These quicklimes, upon addition of water thereto, are converted almost immediately into thick pastes. In conveying the resulting mixture of the quicklime and water to the hydrator or hydration cylinder as, for example, by pumping, the mixture will solidify due to the hydration reaction, and the flow of the mixture to the hydrator will be disrupted.

In order to overcome this problem, resort has been made to increasing the slaking time of the quicklime. For example, resort has been made to calcining the quicklime at higher temperatures and/or for longer periods of time than ordinarily used in order to effect an increase in slaking time, but this procedure results in a reduction in the plasticity and adversely affects other properties of the ultimate hydrated lime. The high temperatures and/or long burning times result in the combination of silicon, iron, aluminum, and other impurities in the quicklime in the form of undesirable substances, for example ferrites or silicates, the presence of which adversely affects the desired physical properties of the resulting hydrated lime, e.g., plasticity, strength, and sand-carrying capacity. In addition, hard-burning involves increased production costs.

It has now been found that these disadvantages can be avoided and that a superior

lime hydrate can be obtained from a fast-acting quicklime in accordance with the present invention which comprises preparing a fast-acting quicklime for hydration by bringing a gaseous reactant consisting of water vapour or mixtures of carbon dioxide and water vapour into contact with a particulate fast-acting quicklime having a hydration time below about one minute, at a temperature to form on the surfaces of said particles a dry film comprising in combination said gaseous reactant and said quicklime, said temperature and the time of contact between said gaseous reactant and said quicklime particles being such that not more than 5×10^{-4} mols of water vapour and not more than 2×10^{-4} mols of carbon dioxide combine with said quicklime for each square metre of surface area of said quicklime, the unreacted portion of said particles consisting essentially of dry quicklime, whereby the slaking time of said quicklime is increased by at least 100%, and thereafter hydrating said particles of quicklime with water essentially in the liquid state to form a substantially dry, powdery lime hydrate.

The process of this invention produces a number of extremely desirable results. One of the most important advantages obtained thereby is a hydrated lime of substantially increased plasticity. As a matter of fact, by means of the present method quicklimes heretofore considered unfit for use as plastic finishing limes, when in the hydrate form, because of their low plasticity may be converted into hydrates having a sufficiently high plasticity, 200 or greater, to be useful as mortars, plasters, and the like. This result is particularly surprising in view of the fact that, if a quicklime is hydrated in an atmosphere of steam, the resulting product is extremely non-plastic and that, if recarbonation takes place during the calcination of limestone, the resulting quicklime, when hydrated, is also non-plastic.

A further benefit obtained by the method of this invention is an increase in the slaking time of fast-acting quicklimes without a reduction in the plasticity of the resulting lime hydrates. By "increase in the slaking time" as used in this specification is meant an increase in the time interval between the initial contact of the quicklime with water and the time at which the hydration reaction has progressed sufficiently to produce steam. This result also is surprising in view of the fact that a reduction in the plasticity of the resulting lime hydrate appears to accompany any increase in the slaking time effected by methods heretofore known. The increase in slaking time is particularly advantageous in those processes where the quicklime is mixed with water and subsequently conveyed to a hydration cylinder as in the process described in United States Patents

2,309,168 and 2,356,736 and briefly discussed above. This increase in slaking time permits transfer of the quicklime-water mixture from the point where the quicklime and the water for hydration are combined to the hydration cylinder without fear of the mixture forming a non-flowable, thick mass. 5

It is believed that, by means of the method of this invention, the quicklime particles become coated at least in part with a thin film, possibly a layer only a few molecules thick, comprising in combination the gaseous reactant and the quicklime. 10

Each particle upon which this film is formed comprises, in addition to the outer shell of the particle, an interior surface portion provided by the porous lattice structure of the quicklime particle which was formed as a result of calcination of the initial limestone. 15

The exact manner in which the gaseous reactant combines with the quicklime particles is not entirely understood. The molecules of the gaseous reactant may be merely adsorbed as such on the surface of the 20 particles, or they may react chemically with the quicklime to form a surface film of calcium carbonate or calcium hydroxide, depending upon the particular gaseous reactant or reactants employed. Thus, the 25 term "combine" as used herein means any physical or chemical association of the gaseous reactant with the surface of the quicklime particles.

This film comprising in combination the 30 gaseous reactant and the quicklime apparently permits water in the liquid phase to penetrate the particles of the quicklime, the interior of which consists essentially of quicklime, so that throughout the interior 35 of each particle water in the liquid phase is present when the quicklime changes from the oxide form to the hydroxide form, a condition believed to contribute materially to the high plasticities obtained in the resulting lime hydrates by means of the 40 method of this invention.

The fast-acting quicklimes which may be employed in the method of this invention comprise any of the well-known types of 45 quicklime, e.g. high calcium quicklimes whose magnesium content generally runs approximately 2% or less but may run as high as 5—10%; high magnesium quicklimes which are usually made from practically pure dolomite and contain approximately 50 55 40% magnesium oxide; and quicklimes which have magnesium contents in between those two magnesium contents and which are usually known as magnesium quicklimes.

Because of the high porosity of quicklime 60 particles, the method of this invention may be satisfactorily carried out with a wide range of sizes of particles. The particles may be as small as those found in fine dusts up to large lump sizes. Preferably, the 65

particles are ground so that the larger particles do not substantially exceed about $\frac{1}{4}$ inch. 70

The quicklime particles should be at a temperature at which the gaseous reactant combines rather readily therewith. The temperature will primarily depend upon the gaseous reactant employed. 75

Where the gaseous reactant consists essentially of carbon dioxide and moisture is present either in the quicklime being treated or in the gaseous state as would be the case in a flue or stack gas, the combining of the gaseous reactant with the quicklime proceeds even at room temperatures. 80

If water vapour is the primary gaseous reactant, the quicklime particles may be at room temperature or at an elevated temperature and preferably at a temperature above the boiling point of water. The preferred range of temperatures where the principal gaseous reactant comprises water vapour is between 250° F. and 450° F. 85

The temperature of the quicklime particles, where the gaseous reactant comprises a mixture of carbon dioxide and water vapour such as that exemplified by a stack gas, is generally the same as that employed where the gaseous reactant comprises water vapour alone. 90

As indicated above, the gaseous reactants employed in accordance with this invention comprise carbon dioxide mixed with water in the gaseous state, e.g., steam, or water vapour alone. These gaseous reactants may 100 be used in combination with other gases which do not react to any measurable degree with the quicklime so as to adversely affect the plasticity of the ultimate lime hydrate. 105

Also, the gaseous reactant may be provided by a flue gas resulting from the combustion of a solid, liquid or gaseous fuel. Satisfactory results are obtained if the flue gas contains that small amount of sulphur dioxide generally found to be present in 110 most flue gases. In this case, the quicklime particles may be contacted directly with the flue gas; preferably the flue gas is at an elevated temperature. Particularly useful is the flue gas from a lime kiln, which flue gas contains 115 substantial portions of both water vapour and carbon dioxide and is readily available to the manufacturer of hydrated lime. Air, particularly moist air, may be used.

Quicklimes vary enormously in both their 120 physical and chemical properties, depending upon the limestone source and the calcination procedure used in making the quicklime. To a large degree the amount of gaseous reactant required for obtaining the highest 125 plasticity in the resulting lime hydrate will depend upon the particular quicklime composition and the particular gaseous reactant employed. However, as a general rule the benefits of this invention can be obtained 130

by using sufficient water vapour so that 0.1×10^{-4} to 5×10^{-4} mol of water combines with the quicklime per square metre of surface area of the quicklime particles. Preferably, sufficient water vapour is used so that 0.5×10^{-4} to 2×10^{-4} mol of water is combined with the quicklime per square meter of surface area of the quicklime particles. This amount of water vapour ordinarily will combine with the quicklime when the quicklime is exposed to dry steam for a period of a few seconds in some cases to a few minutes in others. When the gaseous reactant comprises a mixture of carbon dioxide and water vapour, the respective amounts of each material which combines with the quicklime will depend upon the respective proportions thereof in the gaseous reactant. The amount of carbon dioxide which combines should not exceed about 2×10^{-4} mol per square metre of surface area of the quicklime particles when the water vapour is present in threshold amounts, e.g. 0.1×10^{-4} mol per square metre, and ordinarily will be significantly less than this value due to the presence of greater amounts of water vapour. Preferably, the amount of carbon dioxide which combines will be in the range between 0.1×10^{-4} and 0.5×10^{-4} mol per square metre, and the water vapour combining to the extent of 0.5×10^{-4} to 2×10^{-4} mol per square metre. In most instances a few simple laboratory tests, similar to those of the following specific examples, will readily disclose to the user of this invention the amounts of the particular gaseous reactant required to provide from a given quicklime a lime hydrate having the highest plasticity.

The gaseous reactants should be at elevated temperatures when brought into contact with the quicklime particles. If the gaseous reactant is water vapour, the temperatures should be sufficiently high to ensure that the water vapour remains in the gaseous state, e.g., above 212° F. at atmospheric pressure. The temperature of the gaseous reactants ordinarily should be between 212° F. and 1000° F. although temperatures as high as 1500° F. to 1650° F. may be employed. No particular advantage is to be gained by temperatures substantially above 1000° F. The preferred range of temperatures for the gaseous reactants is 250° F. to 800° F.

After the quicklime particles have been contacted with the gaseous reactant as described above, the quicklime particles may be hydrated by any of the well-known hydration processes. For example, the coated quicklime particles may be hydrated in such well-known hydrators as the Corson, the Kritzer, the Schaffer, the Schulthess, and the Clyde hydrators. If the quicklime particles have been treated under optimum

conditions, an increased plasticity in the lime hydrate product will result regardless of the method of hydration.

According to a preferred mode of operation, the treated quicklime particles are hydrated according to the method of the United States patents discussed above. Thus, the present invention includes hydrating the calcium oxide content and at least a major portion of the magnesia content of the coated quicklime particles under pressure with water in an amount in excess of that which will combine as water of hydration, and drying the resulting slaked quicklime by dispersing the same in an atmosphere under conditions causing the conversion to the vapour phase of the excess water in the resulting dispersed finely divided slaked lime particles. In addition, the method of United States Patent 2,409,546, wherein clustering of the resulting dry powdery lime hydrate is disclosed, is employed. Therefore, the present invention also includes subsequently clustering the resulting dry, powdery lime hydrate by pounding the same between surfaces. By combining the method of this invention with the processes of these patents, even higher plasticities in the resulting lime hydrates are obtained.

The plasticities referred to hereinabove and in the following examples are the plasticities available substantially immediately with water as distinguished from a plasticity requiring hours of soaking to develop.

The surface area of the quicklime particles is determined according to the method described in "Micromeritics of Lime" by Howard R. Staley, published in 1946 by The National Lime Association, United States of America. The degree of surface coating can be determined simply from the surface area and the increase in weight of a given amount of lime after treatment according to the process of the invention.

The following examples are illustrative of the present invention (the screen sizes given are based on the Tyler Standard Sieve Scale):—

EXAMPLE I.

The apparatus employed comprised a chamber with a line connected to its top for delivering steam thereto. The bottom of the chamber was provided with a screened vent. Steam was introduced into the chamber, which contained about 300 grams of an Australian high calcium quicklime, at the same temperature (approximately 83.5% CaO; 3.5% MgO; 8.9% silica as SiO₂; and 1.8% Fe₂O₃ having a particle size of about 97% through a 20-mesh screen, 69% through a 50-mesh screen, 35% through a 100-mesh screen, and 2.5% through a 200-mesh screen). The quicklime particles had a surface area of approximately 1.3

square metres per gram. The steam was introduced at a rate corresponding to 8.8 ml. water per minute for a period of 18 seconds. The quicklime showed a weight increase of 5 approximately 0.1 per cent, which corresponds to water vapour combining with the quicklime to the extent of 0.4×10^{-4} mol per square metre of surface area of the quicklime.

300 g. of quicklime treated as above was 10 placed in a stainless steel beaker; to such quicklime were added 100 g. of water, and the water and quicklime were intimately mixed. This amount of water was determined as that amount theoretically required 15 to completely hydrate the quicklime. Immediately upon addition of the water to the quicklime, the stainless steel beaker was placed in an autoclave containing water in its bottom and sealed from the atmosphere.

20 The water in the bottom of the autoclave did not come into contact with the quicklime and was converted to steam by electric heaters to build up pressure in the autoclave.

25 The pressure in the autoclave increased to about 90 pounds per square inch (gauge) in about 15 minutes, and these conditions were maintained for approximately 20 minutes.

30 At the end of the 20-minute period the pressure in the autoclave was reduced to atmospheric pressure in about one minute; and the sample of the resulting hydrated lime, which was in a dry powdery form, was removed and tested for slaking rate and 35 plasticity.

Plasticities were obtained by means of an Emley plasticimeter: the higher the rating, the more plastic is the hydrated lime.

40 The plasticity of the lime hydrate produced according to this example was 163. A hydrated lime produced from the same quicklime raw material, which had not been subjected to the above steam treatment according to this invention, had a plasticity 45 of 128. The slaking time of the above steam - treated quicklime was about 15 seconds, an increase of about 10 seconds.

EXAMPLE II.

50 Approximately 300 g. of the quicklime of Example I were treated with burnt town gas in the apparatus of that example for a period of one minute. The burnt town gas contained approximately 35 mol per cent of carbon dioxide and 65 mol per cent of 55 water vapour, based on the combined quantity of carbon dioxide and water vapour in the gas. The quicklime showed a weight increase of 0.3 per cent. On the basis that the carbon dioxide and water vapour combine with the quicklime in substantially the same proportions as they are present in the gaseous reactant, 0.3×10^{-4} mol of carbon dioxide and 0.55×10^{-4} mol of water vapour

combined with the quicklime per square metre of surface area of the quicklime. 65

Approximately 600 g. of quicklime thus treated were placed in a hydration cylinder which was provided with a mechanically driven agitator. The cylinder was also provided with a line for delivering water to the cylinder under pressure and a discharge valve for discharging the contents of the cylinder into a porous, bag-type container through which steam and other gases could escape. 70

The cylinder, which was at a temperature of 250° F., was sealed from the atmosphere; and about 433 g. of water were introduced into the cylinder under pressure. This amount of water is 120% in excess of the amount of water necessary to effect complete hydration of the quicklime. 75

Upon addition of the water to the cylinder, the pressure in the cylinder increased; and after approximately 15 seconds the pressure was about 225 p.s.i. (gauge). At the end of about 20 minutes the pressure dropped to about 60 p.s.i. (gauge); the discharge valve was opened, whereby substantially the entire contents of the cylinder comprising hydrated lime, water and steam were discharged into the porous collecting bag. Due to the intrinsic heat of these materials, the water was flashed from the hydrated lime, leaving a dry powdery product. 80

The plasticity of the hydrated lime so produced was obtained by means of an Emley plasticimeter, and the plasticity was found to be 286. A hydrated lime produced from the same quicklime raw material, which had not been treated with carbon dioxide, had a plasticity of 149. The slaking time of the treated quicklime was about 15 seconds as compared to about 5 seconds for the untreated quicklime. 85

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WHAT WE CLAIM IS:—

1. A method for producing dry, powdery hydrated lime which comprises preparing a fast-acting quicklime for hydration by bringing a gaseous reactant consisting of water vapour or mixtures of carbon dioxide and water vapour into contact with a particulate fast-acting quicklime having a hydration time below about one minute, at a temperature to form on the surface of said particles a dry film comprising in combination said gaseous reactant and said quicklime, said temperature and the time of contact between said gaseous reactant and said quicklime particles being such that not more than 5×10^{-4} moles of water vapour and not more than 2×10^{-4} moles of carbon dioxide combine with said quicklime for each square metre of surface area of said quicklime, the unreacted portion of said particles consisting essentially of dry quicklime, whereby the slaking time of said quicklime is increased 110
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by at least 100%, and thereafter hydrating said particles of quicklime with water essentially in the liquid state to form a substantially dry, powdery lime hydrate.

2. A method according to Claim 1, in which said gaseous reactant is provided by a fine gas containing carbon dioxide and water vapour.

3. A method according to Claim 2, in which the quicklime particles are at a temperature between 250° F. and 450° F., and the flue gas is at a temperature between 212° F. and 1000° F.

4. A method according to any one of Claims 1 to 3, in which the calcium oxide content and at least a major portion of the magnesia content of the coated quicklime particles are hydrated under pressure with water in an amount in excess of that which will combine as water of hydration, and the

resulting slaked quicklime is dried by dispersing the same in an atmosphere under conditions causing the conversion to the vapour phase of the excess water in the resulting dispersed finely divided slaked lime particles. 25

5. A method according to Claim 4, which includes subsequently clustering the resulting dry, powdery lime hydrate by pounding the same between surfaces. 30

6. A method for producing a lime hydrate substantially as hereinbefore described.

7. A lime hydrate whenever produced by the method according to any one of Claims 1 to 6. 35

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